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Synthesis of potassium ferrate using residual ferrous sulfate as iron bearing material

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Abstract. This paper summarizes the results obtained during potassium ferrate ($K_2Fe^{VI}O_4$) synthesis which is a high added value material. This compound that contains iron in the rare hexavalent state is becoming a substance of growing importance for the water and effluent treatment industries. This is due to its multi-functional nature (oxidation, flocculation, elimination of heavy metals, decomposition of organic matter, etc.). The most well known synthesis methods for potassium ferrate synthesis are those involving the chemical and/or electrochemical oxidation of iron (II) and (III) from aqueous solutions having a high alkali concentration. These methods are generally characterized by a low Fe^{VI} efficiency due to the reaction of the potassium ferrate with water, leading to the reduction of Fe^{VI} into Fe^{III} . Concerning the work pertinent to this paper, the synthesis of $K_2Fe^{VI}O_4$ was achieved by a simultaneous reaction of two solids (iron sulfate and KOH) and one gaseous oxidant (chlorine). The synthesis process is performed in a rotary reactor at room temperature and the global synthesis reaction is exothermic. The effects of different experimental parameters on the potassium ferrate synthesis are investigated to determine the optimal conditions for the process.

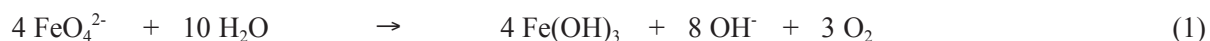
1. Introduction

The denomination "ferrate" is generally attributed to compounds containing iron at oxidation state higher than Fe^{III} . Though the ferrates (IV, V and VI) are cited in the literature, the ferrate (VI) seems to be the best known and the most studied.

The importance of the ferrates' synthesis is related to their considerable and innovating applications in different fields. In aqueous solution, the ferrate ion (FeO_4^{2-}) is reduced, generating both ferric hydroxide precipitate and nascent oxygen, as shown by equation (1). Ferrate is used for water treatment due to its powerful oxidizing capacity (oxidation of organic and mineral materials, biocide agent) and flocculating property of the resulting ferric hydroxide. The ferrate can replace the chlorine

in the pre-oxidation stage of water and partly the iron and aluminum salts [FeCl₃ and Al₂(SO₄)₃] that are used as coagulating and flocculating agents. Furthermore, the decomposition of the ferrate according to equation (1) generates alkaline media favorable to the precipitation of heavy metals into hydroxides. These properties exhibited together by one single compound make the ferrate an ongoing material particularly interesting and valuable for the treatment of water.

The most attractive property of the ferrate ion is its strong oxidizing ability. The redox potentials of the Fe^{VI}/Fe^{III} couples [$E^\circ(FeO_4^{2-}/Fe^{3+})$ and $E^\circ(FeO_4^{2-}/Fe(OH)_3)$] are 2.20 and 0.72 V respectively at pH values equal to 1 and 14. These values are significantly higher than those corresponding to the Mn^{VII}/Mn^{IV} [$E^\circ(MnO_4^-/MnO_2) = 1.679$ and 0.588 V at pH 1 and 14, respectively] or Cr^{VI}/Cr^{III} couples [$E^\circ(Cr_2O_7^{2-}/Cr^{3+}) = 1.33$ V in acidic medium, $E^\circ(CrO_4^{2-}/Cr(OH)_3) = -0.12$ V in alkaline medium]. The use of ferrate as oxidant instead of chromate and/or permanganate is a promising choice from the environmental point of view. One may underline that the oxidants based on chromium and manganese are corrosive, and they are irritant for the skin and for sensitive body organs such as the eyes. The use of chromium compounds as oxidant is also considered toxic for mankind and the environment [1]. As a contrast, ferrate reduction products are not harmful for humans and the environment as they are essentially composed of iron oxy/hydroxides.



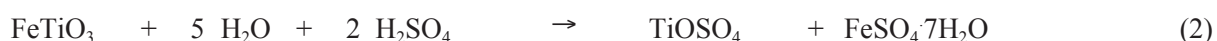
However, the goal of this study is not to focus on the development of alkali ferrates for different applications but to summarize a process developed for K₂Fe^{VI}O₄ synthesis by solid-gas reactions.

2. Materials and Methods

The iron bearing material for the synthesis of potassium ferrate is chosen to be iron sulfate heptahydrate (FeSO₄·7H₂O). The industries of TiO₂ and surface treatment of steel are the main producers of ferrous sulfate and it is considered as a waste for these industries. Titanium dioxide is produced from its raw materials (ilmenite, rutile, anatase, slags, etc.) using "sulfate" and "chloride" process. Ilmenite and titanium slag are used for TiO₂ production using the "sulfate" process. Equations (2) and (3) represent the principal reactions occurring during the treatment of ilmenite to produce TiO₂ in using the sulfate route. Thus, ilmenite is reacting with sulfuric acid generating a solution containing titanyl sulfate and iron sulfate. The solution is treated with metallic iron to reduce ferric ions to ferrous ones, hence avoiding the precipitation of ferric hydroxide. Ferrous sulfate is then crystallized as FeSO₄·7H₂O and is separated from the liquor. Finally, TiOSO₄ is treated to obtain TiO₂.

The major environmental disadvantage of the sulfate process is the large quantities of spent acid and ferrous sulfate generated. The amount of iron sulfate produced depends on the quality of the raw materials used for the titanium dioxide production and can reach up to 6 tons of FeSO₄·7H₂O generated per ton of TiO₂ produced. Since the production of TiO₂ in Europe is essentially made through the "sulfate" method, about 5 million tons of ferrous sulfate heptahydrate are annually generated.

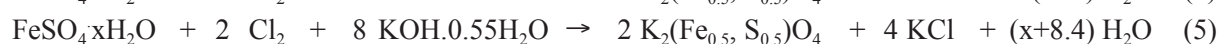
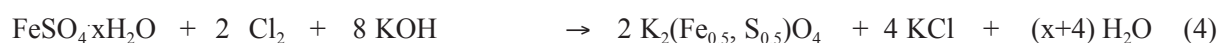
Potassium hydroxide pellets used for the ferrate synthesis had a diameter of about 5 mm. Note that potassium hydroxide contains about 15 % H₂O (by weight). The gaseous reagents (Cl₂, N₂, O₂) used in this research had a purity higher than 99 %.



The main apparatus and experimental procedure for the ferrate synthesis were described previously [2]. The solid sample ($\text{FeSO}_4 \cdot x\text{H}_2\text{O} + \text{KOH}$) was placed in the reactor before a given gas mixture containing chlorine was circulated allowing the ferrate synthesis by the contact of the two solid phases with the gas mixtures ($\text{air} + \text{Cl}_2$ or $\text{N}_2 + \text{O}_2 + \text{Cl}_2$). Though the synthesis was achieved in room conditions, a thermocouple was placed into the sample to measure the temperature increase due to the exothermic nature of the synthesis reactions. The synthesis products, after drying at 65°C , were subjected to Mössbauer spectrometry to determine the Fe^{VI} synthesis efficiency of the process.

3. Results

The potassium ferrate synthesis using $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ and chlorine as oxidant is described by equation (4) producing $(x+4)$ moles of water (x being the amount of structural solvation water moles in the ferrous sulfate). However, potassium hydroxide used for the ferrate synthesis contains about 15 % H_2O . In this condition, the real reaction of ferrate synthesis could be represented by equation (5). This suggests that the amount of water released during the synthesis is high and consequently, it can react with the product and decrease the Fe^{VI} yield. For these reasons, it was suggested to use a partially dehydrated ferrous sulfate for the synthesis of potassium ferrate.



The effects of a good number of parameters (as shown below) on the potassium ferrate synthesis were checked in order to find the best conditions for a high Fe^{VI} efficiency of the process.

- Reactor shape and volume (from 0.2 to 2.5 L),
- Flow rate of gases (from 40 to 700 L/h),
- Type of diluting gas (air and/or N_2),
- Chlorine content in the gas mixtures (2 to 7 % Cl_2),
- Type of iron salt ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $\text{FeSO}_4 \cdot \text{OH}$),
- K/Fe ratio of solids,
- Loading of solids as the reaction progresses,
- Residence time (30 to 120 minutes).

After an optimization of the above-mentioned parameters, a flow-sheet [3] of the potassium ferrate synthesis was proposed (figure 1). According to this flow-sheet, the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ has to be dehydrated at temperatures of about 125°C allowing a control of the water quantity during the potassium ferrate synthesis, and an increase of the reactivity of ferrous sulfate.

The success of the whole process depends on the reactor design and experimental parameters to create the following conditions: (i) a good contact of three substances ($\text{FeSO}_4 \cdot x\text{H}_2\text{O}$, KOH and Cl_2); (ii) a preferential diffusion of KOH towards the reaction zone (iii) a rapid evacuation of the water released from the synthesis reaction; and (iv) a high and uniform heat transfer as the overall synthesis reaction is exothermic. Although the potassium ferrate synthesis was achieved without external heat supply, the reactor temperature increases due to the exothermic nature of the reactions. An increase of the reactor temperature between 45°C to 175°C was observed, depending on the experimental parameters. Good results of potassium ferrate synthesis were obtained for temperatures lower than 100°C with a Fe^{VI} yield as higher as 60 %.

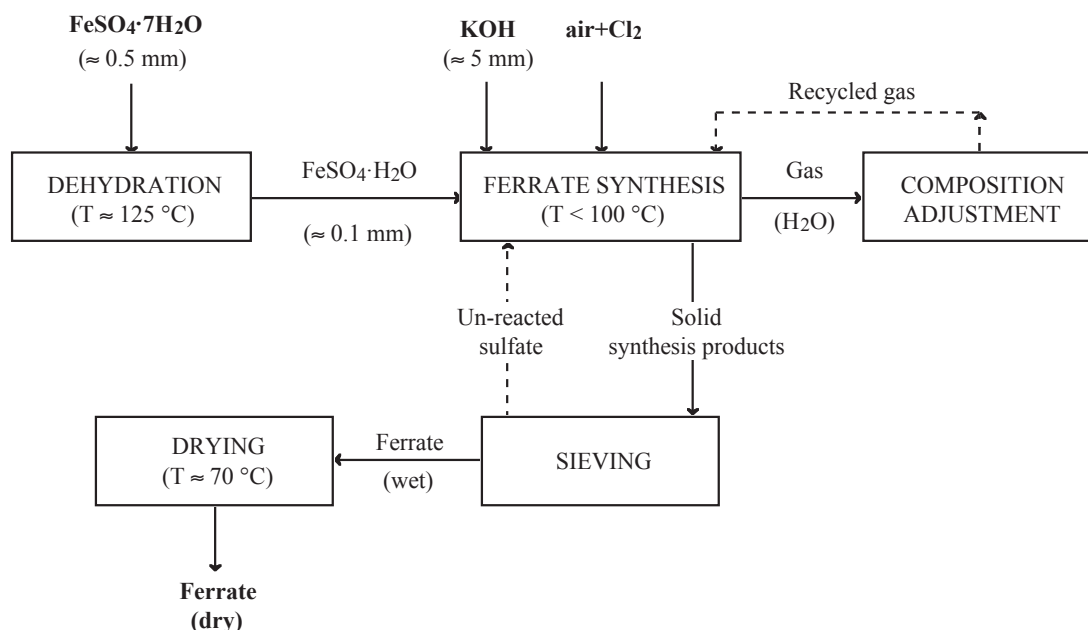


Figure 1. Suggested flow-sheet for the synthesis of potassium ferrate.

The last step of the proposed process consists in the separation of the synthesis products from non reacted ferrous sulfate and drying of the obtained potassium ferrate. The separation of synthesis products from the non reacted ferrous sulfate was facilitated by the important difference of particle size between the ferrate (≈ 5 mm) and that of the ferrous sulfate (≈ 0.1 mm). Thus, a simple sieving of the synthesis product will allow their separation. Ferrate could be dried at temperatures lower than 70 °C. However, in order to not compromise its stability, the drying temperature has to be the lowest possible and never exceed 100 °C.

4. Conclusions

Residual iron sulfate is an appropriate raw material for the preparation of potassium ferrate. The process was achieved in room conditions and the overall synthesis reaction was exothermic. The conversion efficiency of Fe^{II} to Fe^{VI} (Fe^{VI} yield) during potassium ferrate synthesis was higher than or equal to 60 %. This work shows the possibility to transform a waste (iron sulfate) into a useful value added product (potassium ferrate).

Acknowledgments

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